

# 证 明

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## 权 利 要 求 书

1、一种速率可控、低温快速水溶性塑料膜，其特征在于：是将含有磺酸基团或磺酸盐基团的聚合物和聚乙烯醇混合所得到的聚乙烯醇共混聚合物，并按常规的工业化成膜方法制成的塑料膜，所述的磺酸盐基团为磺酸钾基团、或磺酸钠基团、或磺酸铵基团。

2、根据权利要求1所述的速率可控、低温快速水溶性塑料膜，其特征在于：所述的含有磺酸基团或磺酸盐基团的聚合物是由磺酸或磺酸盐单体由游离基聚合反应所得到的含磺酸基团或磺酸盐基团的均聚物或共聚物。

3、根据权利要求1所述的速率可控、低温快速水溶性塑料膜，其特征在于：所述的含有磺酸基团或磺酸盐基团的聚合物是由甲醛和磺酸或磺酸盐单体由缩合聚合反应所得到的含磺酸基团或磺酸盐基团的聚合物。

4、根据权利要求1所述的速率可控、低温快速水溶性塑料膜，其特征在于：所述的含有磺酸基团或磺酸盐基团的聚合物和聚乙烯醇混合所得到的聚乙烯醇共混聚合物中，添加有聚乙烯醇薄膜用的添加剂。

5、根据权利要求1所述的速率可控、低温快速水溶性塑料膜，其特征在于：所述的含有磺酸基团或磺酸盐基团的聚合物和聚乙烯醇混合所得到的聚乙烯醇共混聚合物中，含有磺酸基团或磺酸盐基团的聚合物的用量为0.01-60重量百分比，余量为聚乙烯醇。

6、根据权利要求5所述的速率可控、低温快速水溶性塑料膜，其特征在于：所述的含有磺酸基团或磺酸盐基团的聚合物和聚乙烯醇混合所得到的聚乙烯醇共混聚合物中，含有磺酸基团或磺酸盐基团的聚合物的用量为1-40重量百分比，余量为聚乙烯醇。

7、根据权利要求5或6所述的速率可控、低温快速水溶性塑料膜，其特征在于：所述的含有磺酸基团或磺酸盐基团的聚合物和聚乙烯醇混合所得到的聚乙烯醇共混聚合物中，添加有聚乙烯醇薄膜用的添加剂，该添加剂是含有磺酸基团或磺酸盐基团的聚合物和聚乙烯醇的总重量的0.1-18重量百分比。

8、根据权利要求1所述的速率可控、低温快速水溶性塑料膜，其特征在于：所述的含有磺酸盐基团的聚合物为磺化聚苯乙烯钠盐。

9、根据权利要求8所述的速率可控、低温快速水溶性塑料膜，其特征在于：所述的含有磺酸基团或磺酸盐基团的聚合物和聚乙烯醇混合所得到的聚乙烯醇共混聚合物中，磺化聚苯乙烯钠盐的用量为1-40重量百分比，余量为聚乙烯醇。

10、根据权利要求 9 所述的速率可控、低温快速水溶性塑料膜，其特征在于：所述的含有磺酸基团或磺酸盐基团的聚合物和聚乙烯醇混合所得到的聚乙烯醇共混聚合物中，添加有聚乙烯醇薄膜用的添加剂，该添加剂是磺化聚苯乙烯钠盐和聚乙烯醇的总重量的 0.1-18 重量百分比。

# 说明书

## 速率可控、低温快速水溶性塑料膜

### 技术领域

本发明涉及一种水溶性塑料膜的组成。更确切地表达，本发明所涉及的塑料膜具有水溶速率可以得到控制，在低温甚至在摄氏零度的水中仍能快速溶解的独特性能。更确切地表达，本发明所涉及的水溶性塑料膜由聚乙烯醇和含磺酸基团聚合物或其盐的聚合物所组成。

### 背景技术

目前，水溶聚乙烯醇薄膜的应用越来越广泛，如：用水溶聚乙烯醇薄膜作包装材料，代替现有的包装容器。有毒物品的包装容器在用毕后必须经过处理才能丢弃，由于近来环保要求日趋严格，处理包装容器的费用也必得增加。采用水溶聚乙烯醇薄膜代替包装容器。譬如：杀虫剂、除草剂等，可以使用水溶聚乙烯醇薄膜作为它们的包装材料，就无需处理包装容器。

有些原材料必须精确称量其组份才能有效的使用，譬如：纺织用染料、水泥添加剂、洗涤剂。可预先正确称量，装入水溶聚乙烯醇薄膜袋中，封口。使用时水溶聚乙烯醇薄膜袋可在水中溶解。

传染病房用品需经过消毒才能再使用。将这些用品放入水溶聚乙烯醇薄膜袋中，封口。整袋送入消毒器中消毒，这样，可以避免中间人员因接触这些用品而传染到疾病。

表面装饰水溶转移印刷膜的基材可采用水溶聚乙烯醇薄膜。它要求基材膜水溶快，并且，在印刷层脱离基材膜前，薄膜在水面平整坚挺。

在水溶聚乙烯醇使用上如何控制其水溶速率是一个很关键的问题，尤其是在低温甚至在摄氏零度的水中仍能快速溶解，并能如何控制其水溶速率的问题，直接影响到水溶聚乙烯醇在各个方面的应用，但是，如何控制聚乙烯醇的水溶速率的问题到目前为止都没有得到很好的解决。

已有许多方法和尝试以改进聚乙烯醇薄膜的水溶速率。原理上可归纳为：

1. 使聚合物降解。
2. 改变薄膜的结构。
3. 减少聚乙烯醇分子间的氢键，使它的结构规整度降低。
4. 合成新的聚乙烯醇共聚物。
5. 化学改性聚乙烯醇。

美国专利 6, 071, 618 报导采用高能幅射水溶性塑料薄膜, 使它的水溶速率提高。高能幅射处理的方法是电晕放电、等离子体、紫外照射、爱克斯射线、加马射线、彼达射线, 及高能电子束。高能幅射可以使聚合物降解, 分子量降低, 溶解速率提高。但是, 高能幅射也可以使聚合物产生交联, 使其分子量增大至无限而不熔, 不溶。此外, 高能幅射设备的价格也很昂贵。

美国专利 3, 387, 405 报导将聚乙烯醇水溶液加入凝胶剂, 鼓气形成泡沫结构, 再成型为薄膜。泡沫结构的聚乙烯醇薄膜, 其水溶速率得到提高。由于工艺控制有困难, 生产设备效率低, 因此, 生产成本低。

美国专利 3, 157, 611 报导采用磷酸酯增塑聚乙烯醇薄膜, 可提高它的低温水溶速率。3, 157, 611 专利同时指出, 已有使用甘油、乙二醇、乙酰胺类, 甲酰胺类等添加剂增塑聚乙烯醇薄膜, 以提高它的水溶速率, 但不能提高它的低温水溶速率。这些改进方法都能使聚乙烯醇薄膜的水溶速率有所改进, 但是也有不同的缺点。由于添加剂具有吸湿性, 使聚乙烯醇薄膜的抗湿性差。又由于添加剂容易挥发, 会使聚乙烯醇薄膜失去快速水溶的性能。还由于添加剂易游移至薄膜表面, 不利聚乙烯醇薄膜的水溶速率。磷酸酯和聚乙烯醇的相溶性欠佳, 所以磷酸酯很容易游移到聚乙烯醇薄膜的表面。

美国专利 2, 948, 697 报导采用丙二醇和磷酸酯的组合, 作为聚乙烯醇薄膜的添加剂, 可改进它的高温及低温水溶速率。组合成份和聚乙烯醇的相溶性不佳, 所以很容易游移至薄膜表面, 使水溶速率欠佳。

美国专利 3, 106, 543 报导指出, 用化学改性聚乙烯醇树脂的结构, 改性后的聚乙烯醇水溶液再成型薄膜, 不需要任何添加剂, 就能改进聚乙烯醇薄膜的水溶速率。它的方法是用环氧乙烷部份醚化聚乙烯醇分子中的羟基。改性反应必须在高压下进行。因此, 需要高压反应设备。加上, 聚乙烯醇的反应浓度必须很低, 增加了生产成本。

美国专利 3, 505, 303 报导为提高聚乙烯醇薄膜的水溶速率, 特别是低温水溶速率。它同时指出, 聚乙烯醇通过共聚改性, 只能提高它的高温水溶速率, 不能改善它的低温水溶速率。3, 505, 303 专利提出采用丙烯酰胺, 在碱性条件下经烯烃加成反应, 将丙烯酰胺加成在聚乙烯醇分子的部分羟基上。经此改性的聚乙烯醇所成型的薄膜其低温水溶速率就得到提高。改性反应只能在聚乙烯醇水溶液浓度为 10—20 % 中进行, 加上, 未反应的丙烯酰胺必须回收, 使整个反应成本更加昂贵。

美国专利 6, 071, 618; 曾提及使用高能幅射处理水溶性塑料薄膜, 可提高

它在摄氏零度时的水溶速率，但没有提出具体数据。其它所有上述报导都没有提出可以改善聚乙烯醇薄膜在摄氏零度时的水溶速率。

上述所有的报导都没有提及如何根据实际应用要求，控制聚乙烯醇薄膜的水溶速率。

### 发明内容

本发明的目的是提供一种速率可控、低温快速水溶性塑料膜。可以将水溶性塑料膜的水溶速率得到控制，使水溶性塑料膜的水溶速率无论在高温，低温，甚至在摄氏零度水中，都同样能快速溶解。

为实现上述目的，本发明采取以下技术方案：

一种速率可控、低温快速水溶性塑料膜，是将含有磺酸基团或磺酸盐基团的聚合物和聚乙烯醇混合所得到的聚乙烯醇共混聚合物，并按常规的工业化成膜方法制成的塑料膜，所述的磺酸盐基团为磺酸钾基团、或磺酸钠基团、或磺酸铵基团。所得到的速率可控、低温快速水溶性塑料膜，它的水溶速率在各种温度，甚至在摄氏零度水中都得到提高。本发明的水溶性塑料膜的新组成能提高其水溶速率从来没有被发现，也没有上述背景技术中的报导所提及的各种不同缺点。

用于本发明的含有磺酸基团或它的钾、或钠、或铵盐聚合物可由至少一种下述磺酸或磺酸盐单体由游离基聚合反应所得到的含磺酸基团或它的钾、或钠、或铵盐均聚物或共聚物。

磺酸或磺酸盐单体：

2-氯乙基磺酸及盐；乙烯基磺酸及盐；亚乙基二磺酸及盐；2-甲酰乙基磺酸及盐；1-丙烯-1-磺酸及盐；1-丙烯-2-磺酸及盐；2-甲酰-1-甲基乙烯基磺酸及盐；1-羧基-2-甲基乙烯基磺酸及盐；2-甲基-1，3 丙烯二磺酸及盐；1-丁基-1-磺酸及盐；1-羧基-2，2-二甲基乙烯基磺酸及盐；1-戊烯-1-磺酸及盐；1-己烯-1-磺酸及盐；2（对硝基苯）乙烯基磺酸及盐；2-苯基乙烯基磺酸及盐；2（对羟基苯）乙烯基磺酸及盐；2（2-氨基苯）乙烯基磺酸及盐；1-甲基-2-苯基乙烯基磺酸及盐，2（对甲氧基苯基）乙烯基磺酸及盐；4-苯基-1，3-丁二烯磺酸及盐；2（对-乙酰氨基苯）乙烯基磺酸及盐；

3-氯烯丙基磺酸及盐；烯丙基磺酸及盐；1-羟基烯丙基磺酸及盐；2-腈基烯丙基磺酸及盐；3-氯-2-丁烯磺酸及盐；3-氯甲基烯丙基磺酸及盐；1-羧基丙基磺酸及盐；3-羧基烯丙基磺酸及盐；烯丙酰氨基乙磺酸及盐；2-甲基烯丙酰环氧乙烷磺酸及盐；2-丙稀酰胺-2-甲基丙烷磺酸及盐；甲基丙烯酸-2-磺基乙基酯；4-

(N-苯磺酸) 顺丁烯二酰亚胺及盐; 丙烯酸 N-2-羟乙基-哌嗪-N'-乙基磺酸酯及盐; 乙烯基磺基三甲胺乙内酯咪唑及盐; 甲基烯丙基磺酸及盐; 2-亚甲基-4, 4-二甲基-1, 3-二磺酸戊烯; 4-亚甲基-4, 4-二甲基戊烯磺酸及盐; 1-羧基-3-苯基烯丙基磺酸及盐; 3-苯基烯丙基磺酸及盐; 2-苯基烯丙基磺酸及盐; 2-(对甲基苯氧基) 烯丙基磺酸及盐; 3-苯氧基甲基烯丙基磺酸及盐; 4-亚甲基-2, 2, 6, 6-四甲基-3, 5-二磺酸庚烯; 丙烯酸 2-磺基乙酯及盐; 马来酸 2-磺基乙酯及盐; 丙烯酸 3-磺基丙酯及盐; 甲基丙烯酸 3-磺基丙酯及盐; 马来酸 3-磺基丙酯及盐; 甲基丙烯酸 2-磺基-1-(磺甲基) 乙酯及盐; 甲基丙烯酸 4-磺基丁基酯及盐; 2-(丙烯酰氧甲基)-C-呋喃磺酸及盐; 富马酸双-2-磺基乙酯及盐; 衣康酸 3-磺基丙酯; 丙烯酸对磺基苯酯及盐; 2-(2-甲基丙烯酰氧甲基呋喃磺酸及盐; 衣康酸双(2-磺基乙基) 酯及盐; 甲基丙烯酸对磺基苯酯及盐; 马来酸双(3-磺基丙基) 酯及盐; 马来酸双(2-磺基丙基) 酯及盐; 富马来酸双(2-磺基丙基) 酯及盐; 5-甲基-2-(甲基烯丙基) 苯磺酸及盐; 衣康酸双(2-磺基甲基) 酯及盐; 芳基-(2-丙烯酰氧乙氧基)-2-萘磺酸及盐; 芳基-(2-甲基丙烯酰氧乙氧基) 萘磺酸及盐; 衣康酸十二酯-4-磺基丙基酯及盐; 衣康酸十二酯-4-磺基丁基酯及盐; N-丙烯酰牛磺酸及盐; 烯丙基硫乙基磺酸及盐; 烯丙基氧乙基磺酸及盐; 烯丙基氧丙基磺酸及盐; N-烯丙基-N-甲氨基乙烷-磺酸及盐; N-(甲基丙烯酰胺甲基) 磺基乙酰胺及盐; 乙烯基氧苯基磺酸及盐; 烯丙基氧苯基磺酸及盐; N-(对-磺基苯) 甲基丙烯酰胺及盐; 对-[(2-乙烯基磺酰基) 氧乙基] 苯磺酸及盐; N-甲基-N-(2-乙烯基磺酰基乙基)-对-(磺基) 苄胺及盐; 二氯苯乙烯磺酸及盐; 2-氯苯乙烯磺酸及盐; 对苯乙烯磺酸及盐; 苯乙烯磺酸及盐; 对磺基月桂酸及盐; 乙烯基甲苯磺酸及盐; 2-甲基苯乙烯磺酸及盐;

用于本发明的含磺酸基团或它的钾、或钠、或铵盐聚合物可由至少一种上述磺酸或磺酸盐单体由游离基聚合反应所得到的含磺酸基团或它的钾、或钠、或铵盐均聚物或共聚物。其中, 游离基聚合引发剂可采用常用的引发剂: 偶氮二异丁腈; 乙酰基过氧化物; 苯甲酰过氧化物; 叔丁基过氧化物; 异丙基过氧化物; 叔丁基氢过氧化物; 异丙苯基氢过氧化物; 过氧化氢-硫酸亚铁。

由上述一种磺酸或磺酸盐单体通过游离基聚合反应所得到的含磺酸基团或钾、或钠、或铵盐的均聚聚合物是只有一种单体聚合而成的聚合物。由至少一种上述磺酸或磺酸盐单体和乙烯基单体通过游离基聚合反应所得到的含磺酸基团或钾、或钠、或铵盐的共聚聚合物是由几种单体聚合而成的聚合物。其中, 共聚聚合物可以由两种单体聚合而成的聚合物, 称为两元单体共聚体; 也可

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以是由三种单体聚合而成的聚合物，称为三元单体共聚体，以此类推，还可以是其它的多元单体共聚体。

上述的游离基聚合方法可以采用现已有的工业化的溶液聚合，乳液聚合，本体聚合及分散聚合。

用于本发明的含有磺酸基团或它的钾、或钠、或铵盐聚合物可由甲醛和至少一种下述磺酸或磺酸盐单体由缩合聚合反应所得到的含磺酸基团或它的钾、或钠、或铵盐聚合物。

磺酸或磺酸盐缩聚单体：

甲苯胺磺酸；氨基苯酚磺酸；2-氨基-4-氯苯酚磺酸；2-氨基-1-萘磺酸；1-氨基，8-萘酚-3，5 二磺酸；氨基萘三磺酸；苯胺-2，5，二磺酸；二氨基二磺酸；苯酚磺酸，氨基萘酚二磺一酸，氨基二苯胺甲烷磺酸。

含磺酸基团或它的钾、或钠、或铵盐聚合物可由聚合物经工业化常用的磺化剂及烷基磺化剂通过磺化及烷基磺化反应而得到。常用磺化剂及烷基磺化剂有浓硫酸；发烟硫酸；三氧化硫；氯磺酸；磺内酯；乙酰硫酸酯。所得磺化聚合物有磺化聚苯乙烯；磺化聚砒；磺化三聚氰胺树脂；磺化酚醛树脂；磺化脲醛树脂；磺化萘甲醛树脂；磺甲基纤维素；磺化聚氨脂；磺化聚丙二醇；磺化聚乙二醇。

本发明速率的可控、低温快速水溶性塑料膜，可以含有常用的，已有报导的添加剂，譬如：增塑剂，抗氧剂，脱模剂，防结剂，增滑剂，消泡剂，润滑剂，表面活性剂，及无机填充剂。使用这些添加物并不限止本发明。

在聚乙烯醇和含磺酸基团或它的钾、或钠、或铵盐聚合物组成的重量百分比中，含磺酸基团或它的钾、或钠、或铵聚合物的用量为 0.01-60 重量百分比；优选用量为 0.1-50 重量百分比；更优选用量为 1-45 重量百分比；最优选用量为 1-40 重量百分比。

在本发明的速率可控、低温快速水溶性塑料膜中，所述的含有磺酸基团或磺酸盐基团的聚合物和聚乙烯醇混合所得到的聚乙烯醇共混聚合物中，添加有聚乙烯醇薄膜用的添加剂。该添加剂是含有磺酸基团或磺酸盐基团的聚合物和聚乙烯醇的总重量的 0.1-18 重量百分比。

在本发明的速率可控、低温快速水溶性塑料膜中，所述的含有磺酸基团或磺酸盐基团的聚合物的数均分子量为 18,000-26,000，优选数均分子量为 19,000-23,000。所述的聚乙烯醇树脂的数均分子量 7,000-13,000，优选数均分子量为 8,000-11,000。



本发明的速率可控、低温快速水溶性塑料膜是按常规的工业化成膜方法制成的，含有磺酸基团或磺酸盐基团的聚合物和聚乙烯醇混合可以溶液混合、或熔融混合、或液固混合得到的聚乙烯醇共混聚合物。一般通过熔融混合，用造粒机造粒，然后用塑料挤出吹膜机进行挤出吹膜，造粒及挤出吹膜的加工温度均为 185-200℃，再用分切机将薄膜分切，用复卷机复卷，最后验收、包装为成品。所使用的造粒机、塑料挤出吹膜机、分切机、复卷机均为普通设备。

在本发明的速率可控、低温快速水溶性塑料膜中，所述的含有磺酸盐基团的聚合物优选为磺化聚苯乙烯钠盐。

在聚乙烯醇和磺化聚苯乙烯钠盐组成的重量百分比中，磺化聚苯乙烯钠盐的用量为 0.01-60 重量百分比；优选用量为 0.1-50 重量百分比；更优选用量为 1-45 重量百分比；最优选用量为 1-40 重量百分比。

在本发明的速率可控、低温快速水溶性塑料膜中，所述的磺化聚苯乙烯钠盐和聚乙烯醇混合所得到的聚乙烯醇共混聚合物中，添加有聚乙烯醇薄膜用的添加剂。该添加剂是磺化聚苯乙烯钠盐和聚乙烯醇的总重量的 0.1-18 重量百分比。

在本发明的速率可控、低温快速水溶性塑料膜中，所述的磺化聚苯乙烯钠盐的数均分子量为 18,000—26,000，优选数均分子量为 19,000—23,000。所述的聚乙烯醇树脂的数均分子量 7,000—13,000，优选数均分子量为 8,000—11,000。

本发明的速率可控、低温快速水溶性塑料膜由聚乙烯醇和含磺酸基团或它的钾或钠、或铵盐聚合物组成。它可称为聚乙烯醇，磺基聚合物共混聚合物膜。共混聚合物又称为“塑料合金”。新的组成是一种新的“塑料合金”。

对本发明的新组成所具有的速率可控，低温快速的机理并不清楚了解。但是，通过试验我们可以得到这样的结果，聚苯乙烯本身是不溶解于水的，而由于磺酸基团或它的钾或钠、或铵盐的引入使它能溶解于水。众所周知，磺基聚合物能改善塑料膜的印刷性能。其原因是磺酸基团或它的盐能提高亲水性及降低表面活化能。这两者都有利于水溶性塑料膜的水溶速率。

### 具体实施方式

#### 实施例 1

按下述重量百分比备料

|          |        |
|----------|--------|
| 聚乙烯醇     | 90Wt%  |
| 磺化聚苯乙烯钠盐 | 10 Wt% |

其中，聚乙烯醇的数均分子量为 7, 000—13, 000；磺化聚苯乙烯钠盐的数均分子量为 18, 000—26, 000。

将上述配比原料混合，用造粒机造粒，然后用塑料挤出吹膜机进行挤出吹膜，造粒及挤出吹膜的加工温度均为 200℃，再用分切机将薄膜分切，用复卷机复卷，最后验收、包装为成品。

实施例 2

除原料的重量百分比、造粒及挤出吹膜的加工的温度不同于实施例 1 外，其余的都和实施例 1 相同。

原料重量百分比：

聚乙烯醇 80Wt%

磺化聚苯乙烯钠盐 20 Wt%

造粒及挤出吹膜的加工温度均为 195℃。

实施例 3

除原料的重量百分比、造粒及挤出吹膜的加工的温度不同于实施例 1 外，其余的都和实施例 1 相同。

原料重量百分比：

聚乙烯醇 70Wt%

磺化聚苯乙烯钠盐 30 Wt%

造粒及挤出吹膜的加工温度均为 190℃。

比较例 1

除原料采用 100Wt%的聚乙烯醇，及造粒及挤出吹膜的加工的温度不同于实施例 1 外，其余的都和实施例 1 相同。造粒及挤出吹膜的加工温度均为 200℃。

水溶速率的测定实验 1

对上述实施例 1、2、3 和比较例 1 所制成的薄膜，进行水溶速率的测定，其测定的方法是，将一定长度、宽度、及厚度的薄膜（本实验中，薄膜长 4 厘米、宽 1 厘米、厚 0. 03 毫米）放入 500 毫升的玻璃烧杯中，玻璃烧杯盛有 250 毫升，在 15℃ 温度的水。搅拌使玻璃烧杯中的水保持运动。从薄膜接触水开始，至用肉眼看到薄膜完全溶解为止，这一段时间就是薄膜的水溶速率。以秒计算。实施例 1、2、3 和比较例 1 所制成的薄膜的水溶速率见表 1：

表 1

|          | 薄膜组份重量百分比 (Wt%) |    | 水温为 15℃ 条件下<br>水溶速率 (秒) |
|----------|-----------------|----|-------------------------|
|          | A               | B  |                         |
| 比较例 1 薄膜 | 100             |    | 14.2                    |
| 实施例 1 薄膜 | 90              | 10 | 10.2                    |
| 实施例 2 薄膜 | 80              | 20 | 8                       |
| 实施例 3 薄膜 | 70              | 30 | 3                       |

A=聚乙烯醇树脂，数均分子量 7,000—13,000。

B=磺化聚苯乙烯钠盐，数均分子量为 18,000—26,000。

以上实验数据表明，将比较例 1 薄膜即聚乙烯醇薄膜的水溶速率作为基准，样品薄膜的水溶速率，随着本发明的磺化聚苯乙烯钠盐用量的增加，样品薄膜的水溶速率亦增加。实施例 1 薄膜的水溶速率的增加，是基准的 1.4 倍。实施例 2 薄膜的水溶速率的增加，是基准的 1.8 倍。实施例 3 薄膜的水溶速率的增加，是基准的 4.8 倍。

#### 实施例 4

除原料的重量百分比、并加入添加剂、和造粒及挤出吹膜的加工的温度不同于实施例 1 外，其余的都和实施例 1 相同。

原料重量百分比：

聚乙烯醇 91Wt%

磺化聚苯乙烯钠盐 9 Wt%

再加入上述原料的总量的 16 Wt%的添加剂，其中，丙二醇为 12.6Wt%，碳 14—16 的烯烃磺酸钠为 1.7Wt%，油基二羟乙基酚胺为 1.7Wt%。造粒及挤出吹膜的加工温度均为 195℃。

#### 比较例 2

除原料采用 100Wt%的聚乙烯醇，并加入添加剂、和造粒及挤出吹膜的加工的温度不同于实施例 1 外，其余的都和实施例 1 相同。

再加入上述 100Wt%的聚乙烯醇原料的总量的 16 Wt%的添加剂，其中，丙二醇为 12.6Wt%，碳 14—16 的烯烃磺酸钠为 1.7Wt%，油基二羟乙基酚胺为 1.7Wt%。造粒及挤出吹膜的加工温度均为 198℃。

#### 水溶速率的测定实验 2

对上述实施例 4 和比较例 2 所制成的薄膜，进行水溶速率的测定，其测定的方法除水温不同外，其余的都和水溶速率的测定实验 1 相同。本实验的水温为 25℃。实施例 4 和比较例 2 所制成的薄膜的水溶速率见表 2：

表 2

|       | 薄膜组份重量百分比 (Wt%) |   |    | 水温为 25℃ 条件下<br>水溶速率 (秒) |
|-------|-----------------|---|----|-------------------------|
|       | A               | B | C  |                         |
| 比较例 2 | 100             |   | 16 | 8.4                     |
| 实施例 4 | 91              | 9 | 16 | 4                       |

A=聚乙烯醇树脂, 数均分子量 7,000—13,000。

B=磺化聚苯乙烯钠盐, 数均分子量为 18,000—26,000。

C=添加剂, 其中, 丙二醇为 12.6Wt%, 碳 14—16 的烯烴磺酸钠为 1.7Wt%, 油基二羟乙基酚胺为 1.7Wt%。碳 14—16 的烯烴磺酸钠和油基二羟乙基酚胺为表面活性剂。

实验数据表明, 添加了聚乙烯醇薄膜用的添加剂的本发明的水溶性塑料膜仍然具有速率可控、低温快速水溶性的特性。在摄氏 25 度时, 以比较例 2 薄膜即添加了添加剂的聚乙烯醇薄膜的水溶速率为基准, 实施例 4 薄膜即添加了添加剂的本发明的水溶性塑料膜的水溶速率的增加, 是基准的 2.1 倍。

#### 水溶速率的测定实验 3

对上述实施例 4 和比较例 2 所制成的薄膜, 进行水溶速率的测定, 其测定的方法除水温不同外, 其余的都和水溶速率的测定实验 1 相同。本实验的水温为 0℃。实施例 4 和比较例 2 所制成的薄膜的水溶速率见表 3:

表 3

|       | 薄膜组份重量百分比 (Wt%) |   |    | 水温为 0℃ 条件下<br>水溶速率 (秒) |
|-------|-----------------|---|----|------------------------|
|       | A               | B | C  |                        |
| 比较例 2 | 100             |   | 16 | 22.4                   |
| 实施例 4 | 91              | 9 | 16 | 9.4                    |

A=聚乙烯醇树脂, 数均分子量 7,000—13,000。

B=磺化聚苯乙烯钠盐, 数均分子量为 18,000—26,000。

C=添加剂, 其中, 丙二醇为 12.6Wt%, 碳 14—16 的烯烴磺酸钠为 1.7Wt%, 油基二羟乙基酚胺为 1.7Wt%。碳 14—16 的烯烴磺酸钠和油基二羟乙基酚胺为表面活性剂。

实验数据表明, 添加了聚乙烯醇薄膜用的添加剂的本发明的水溶性塑料膜仍然具有速率可控、低温快速水溶性的特性。在摄氏 0 度时, 以比较例 2 薄膜

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即添加了添加剂的聚乙烯醇薄膜的水溶速率为基准，实施例 4 薄膜即添加了添加剂的本发明的水溶性塑料膜的水溶速率的增加，是基准的 2.4 倍。

综上所述，本发明的速率可控、低温快速水溶性塑料膜具有以下的特点：

1、通过对组合重量的不同配比可以调控薄膜的水溶速率，即通过含磺酸基团或它的钾或钠、或铵盐聚合物在组合物中的重量百分比调控薄膜的水溶速率，也就是说通过磺基聚合物量的多少控制薄膜的水溶速率的快慢。

2、塑料膜在摄氏零度的水中也可以快速溶解。

本发明的速率可控、低温快速水溶性塑料膜根据上述的特点即将塑料膜放在水中、或放在水的表面在可以控制的一定时间内塑料膜具有溶解的特性，采用将塑料膜放在水中、或放在水的表面等进行溶解的方法，作为包装材料、包装袋、表面装饰水溶转移印刷膜的基材等的应用。

**CERTIFIED TRANSLATION OF CHINESE APPLICATION  
SERIAL NO. 03 1 09627.1, FILED APRIL 9, 2003.**

**(TRANSLATOR'S CERTIFICATION IS ON LAST PAGE)**

## Water soluble polymeric films with controllable and great solving rate

### ABSTRACT

The water soluble films of this invention are prepared from the novel polymer blends of polyvinyl alcohol and polymers containing sulfo group. All conventional film forming processes can be used to produce said films. In said polymer blends there is 0.1-60wt% of polymers containing sulfo group.

Said films have unique characteristics. Their water solving rates can be controlled by varying the compositions of said polymer blends and are great at low temperature, even at the temperature of 0° C.

Said films can be used as packaging materials and immersion printing films.

### FIELD OF THE INVENTION

This invention relates to the compositions of the novel polymer blends used for preparing films, particularly for preparing water soluble films, by conventional film forming processes. The solving rates of said films can be controlled and are great at high, ambient and low temperature, even at the temperature of 0° C.

Said polymer blends consist essentially of (1) polyvinyl alcohol and (2) polymers containing sulfo group.

### BACKGROUND OF THE INVENTION

Considerable interest has been evidenced recently in using polyvinyl alcohol (PVOH) water soluble films to produce packaging containers or bags. The packaging containers or bags contaminated by toxic or harmful materials such as biocides, preservatives, bleach agents, fertilizers and detergents must be disposed in an environmental safe way. Under the increasing pressure of environmental regulations, it frequently is extremely difficult and expensive to dispose the used containers or bags just mentioned. For the sake of safety, it is highly desirable to use water soluble polymer to produce packaging containers or bags for holding toxic or harmful materials. Most of these chemicals are in powder or dust form. When a user is handling them, he/she may breathe in their dust particles floating in the air. Water soluble packaging bags can prevent the dust particles from floating in the air: when a chemical is needed, it is immersed in water with its packaging bag, and the bag dissolves in water with its content. Pollution problem is eliminated.

For accuracy or convenience of using the chemicals, they can be packaged in unit containers or bags with pre-determined quantity. It is desirable for the market to provide dye, detergent or cement etc. in unit containers or bags. The use of such containers or bags permits accurate amount of the packaged chemicals to be used without handling the chemicals directly to prevent the users from exposing to the chemicals. Said films are suitable materials to prepare the above mentioned unit containers or bags. When it is needed, the container or bag is immersed in water and its content dissolves in water.

For the sake of health, the used articles such as bed cloths and blankets etc. from hospitals, particularly from hospitals of infectious diseases have to be sterilized before they can be reused. It

is extremely important to prevent the workers in charge to handle them from contacting and exposing to them. The containers or bags prepared from said films can be used as containers holding the used articles, which can be put into the sterilizer directly without opening them to eliminate the possible contact of any infectious disease bacteria.

Water soluble containers or bags prepared from said films are particularly valuable where their contents are toxic or are not permitted to be touched.

Said films are widely used in immersion printing processes. This is a unique process for decorating products with complex curving surfaces. Said films can suitably be used as carriers of immersion printing plates. In immersion printing processes, water solving rate which can be controlled and stiffness are both very important to the films floating on the water surface.

Water soluble films with the characteristics of controllable solving rate and great solving rate at low temperature, even at the temperature of 0°C are most needed in the market. Said films are just the commodities most needed in the market.

Many techniques applied to polyvinyl alcohol in order to raise its water solving rate have been investigated. Theoretically, they can be summarized as follows:

1. degradation of the polymer;
2. design of film structure;
3. new copolymers of polyvinyl alcohol; and
4. modification of polyvinyl alcohol.

US 6,071,618 discloses a process for raising the solving rate of a water soluble polyvinyl alcohol film. A polymeric film comprises at least one irradiated water soluble layer. In an irradiation process, the film is subjected to an energetic radiation treatment such as corona discharge, plasma, flame, ultraviolet, X-ray, gamma ray, beta ray and high energy electron treatment. It is known that the molecular weight of the polymer under radiation treatment will be reduced because of degradation of the polymer during the period of irradiation, will raise the solving rate of the polymer. It is also known that the molecular weight of the polymer will be increased because of cross linking between polymers during the period of irradiation, will lower the solving rate of the polymer. Irradiation equipments and processes are very expensive.

US 3,387,405 discloses a foam structure film of polyvinyl alcohol. A polyvinyl solution containing gelling agents is mixed with air bubbles under pressure. The foam is dried into a cellular film with improved water solving rate. It is a slow process and the gelling condition is difficult to be controlled. The cost is high.

US 3,157,611 discloses that the polyvinyl alcohol film plasticized by phosphate esters is improved in its cold water solving rate. It also indicates that many plasticizers such as glycerin, ethylene glycol, ethanol acetamide and ethanol formamide are added into polyvinyl alcohol to produce polymeric materials with improved water solving rate, but they are not effective enough in producing polymeric materials with improved cold water solving rate.

The above mentioned plasticizers are suffering the following disadvantages: they are humectants



which absorb moisture in high humidity conditions to make them become tacky and weak; they are volatile so that they are easy to migrate to their surface. All these disadvantages will affect the water solving rate and other physical properties of the film. Therefore that phosphate esters are not well compatible with polyvinyl alcohol results in the former tending to migrate to the surface of the latter.

US 2,948,697 discloses that polyvinyl alcohol films plasticized by combination of polypropylene glycol and phosphate esters are improved in their water solving rates both at high and low temperatures. But they still suffer two problems: poor compatibility between polyvinyl alcohol and plasticizers; and plasticizers migration to the surface of the films.

US 3,106,543 discloses a polyvinyl alcohol modification method: an ethylene oxide reacts with aqueous polyvinyl alcohol solution to obtain a hydroxyethylated polyvinyl alcohol. The films prepared from the modified polyvinyl alcohol do not contain any plasticizers. Because the process must be carried out in extremely dilute aqueous polyvinyl alcohol solution in an autoclave. The process is expensive.

US 3,505,303 discloses a film made of modified polyvinyl alcohols, which is clear, colorless and readily soluble in cold water. It indicates that the solubility of a film can be raised by modifying polyvinyl alcohol through copolymerization, but the solubility of a film in cold water can not be raised. The films prepared from US 3,505,303 have great cold water solving rate. Under alkaline condition, acryl amide is added to some of the hydroxyl groups of the polyvinyl alcohol molecules by alkene addition reaction. Because the concentration of the polyvinyl alcohol solution is 10-20%, the process is expensive. In addition, the acryl amides must be recovered. An extra cost must be paid.

US 6,071,618 indicates that the water solving rates of the polymeric films, to which it relates, can be raised at the temperature of 0° C. No other US patents mentioned above has mentioned this subject.

None of the above mentioned US patents have mentioned the subject about the controllability of water solving rate.

#### DESCRIPTION OF INVENTION

The present invention provides various polymer blends of polyvinyl alcohol and polymers containing sulfo group. The polymeric films prepared from said blends are characterized by the water solving rate which can be controlled and great water solubility at low temperature, even at the temperature of 0° C.

Said polymers containing sulfo group comprise the polymers formed by free-radical homo-polymerization or copolymerization of the following sulfonate monomers.

Sulfonate monomers:

2-Chloroethylene Sulfonic Acid and its Salt  
 Ethylenesulfonic Acid and its salt  
 Ethylenedisulfonic Acid and its salt  
 1-Nitriloethylenesulfonic Acid and its Salt  
 2-Formylethylenesulfonic Acid and its Salt  
 1-Carboxyethylenesulfonic Acid and its Salt  
 1-Propene-1-Sulfonic Acid and its salt  
 1-Propene-2-Sulfonic Acid and its salt  
 2-Formyl-1-Methylethylene Sulfonic Acid and its salt  
 1-Carboxy-2- Methylethylene Sulfonic Acid and its Salt  
 2- Methyl-1,3-Propenedisulfonic Acid and its salt  
 1-Butene-1-Sulfonic Acid and its salt  
 1-Carboxy-2,2-dimethyl-Ethylene Sulfonic Acid and its Salt  
 1-Pentene-1-Sulfonic Acid and its salt  
 1-Hexene-1-Sulfonic Acid and its salt  
 2-(p-Nitrophenyl) Ethylene Sulfonic Acid and its salt  
 2-Phenylethylene Sulfonic Acid and its salt  
 2-(p-Hydroxyphenyl) Ethylene Sulfonic Acid and its salt  
 2-(2-Aminophenyl) Ethylene Sulfonic Acid and its salt  
 1- Methyl-2-Phenylethylene Sulfonic Acid and its salt  
 2- (p-Methoxyphenyl) Ethylene Sulfonic Acid and its salt  
 4-Phenyl-1,3-Butadiene Sulfonic Acid and its salt  
 2-(p-Acetamidophenyl) Ethylene Sulfonic Acid and its salt

3-Chloroallyl Sulfonic Acid and its salt  
 Allyl Sulfonic Acid and its salt  
 1-Hydroxyallyl Sulfonic Acid and its salt  
 2-Cyanoallyl Sulfonic Acid and its salt  
 3-Chloromethallyl Sulfonic Acid and its salt  
 1-Carboxyallyl Sulfonic Acid and its salt  
 3-Carboxyallyl Sulfonic Acid and its salt  
 Methallyl Sulfonic Acid and its salt  
 2-Methylene-4,4-Dimethyl-1,3-Disulfo-pentene Acid and its salt  
 4-Methylene-4,4-Dimethyl Pentene Sulfonic Acid and its salt  
 1-Hydroxy-3-Phenylallyl Sulfonic Acid and its salt  
 3-Phenylallyl Sulfonic Acid and its salt  
 2-Benzylallyl Sulfonic Acid and its salt  
 2-(p-methylphenoxy)-Allyl Sulfonic Acid and its salt  
 3-Phenoxymethallyl Sulfonic Acid and its salt  
 4-Methylene-2,2,6,6-tetramethyl-3,5-Disulfoheptene

2-Sulfoethyl Acrylate and its Salt  
 2-Sulfoethyl Maleate and its Salt  
 3-Sulfopropyl Acrylate and its Salt  
 2-Sulfonyl Methacrylate and its Salt  
 2-Sulfo-1-(Sulfomethyl) Ethyl Methacrylate and its Salt  
 3-Sulfopropyl Maleate and its Salt  
 4-Sulfobutyl Methacrylate and its Salt  
 2-(Acyloxymethyl)-C-Sulfuran and its Salt  
 Bis-2-Sulfoethyl Fumarate and its Salt  
 3-Sulfopropyl Itaconate and its Salt  
 p-Sulfophenyl Acrylate and its Salt  
 2-(2-methylacryloxymethyl)-Sulfofuran and its Salt  
 Bis(2-Sulfoethyl) Itaconate and its Salt  
 p- Sulfophenyl Methacrylate and its Salt  
 Bis(3-Sulfopropyl) Maleate and its Salt  
 Bis(3-Sulfopropyl) Fumarate and its Salt  
 Bis(2-Sulfopropyl) Maleate and its Salt  
 Bis(2-Sulfopropyl) Fumarate and its Salt  
 5-Methyl-2-(Methallyloxy) Benzene Sulfonic Acid and its Salt  
 Bis(2-Sulfopropyl) Itaconate and its Salt  
 Ar-(2-Acryloyloxyethoxy)-2-Naphthalene Sulfonic Acid and its Salt  
 Ar-(2-Methacryloyloxyethoxy)-Naphthalene Sulfonic Acid and its Salt  
 Dodecyl-4- Sulfopropyl Itaconate and its Salt  
 Dodecyl-4- Sulfobutyl Itaconate and its Salt  
 N-Acryloyl Taurine and its Salt  
 Allylthioethyl Sulfonic Acid and its salt  
 Allyloxyethyl Sulfonic Acid  
 Allyloxy Propene Sulfonic Acid and its salt  
 N-Allyl-N-Methylaminoethane Sulfonic Acid and its salt  
 N-(Methacrylamidomethyl)-Sulfoacetamide and its Salt  
 Vinyloxybenzene Sulfonic Acid and its salt  
 Allyl Oxybenzene Sulfonic Acid  
 N-(p-Sulfophenyl) Methacrylamide and its salt  
 p-[(2-Vinylsulfonyl)ethoxy]-Benzene Sulfonic Acid and its salt  
 N-Methyl-N-(2-Vinylsulfonyl-Ethyl)-p-(Sodiumsulfo) Benzyl Amine and its Salt

Dichlorostyrene Sulfonic Acid and its salt  
 2-Chlorostyrene Sulfonic Acid and its salt  
 p-Styrene Sulfonic Acid and its salt  
 Styrene Sulfonic Acid  
 p-Sulfonic Acid and its salt  
 Vinyltoluene Sulfonic Acid and its salt

## 2-Methyl Styrene Sulfonic Acid and its salt

Said polymers containing sulfo group comprise the polymers formed by free-radical copolymerization of , at least, one of the sulfonate monomers and the following olefinic comonomers.

Olefinic comonomers:

Acrylic Acid and its Salt

Methyl Acrylic Acid and its Salt

Acrylates

Methacrylates

Acrylamide

Methylacrylamide

Vinyl Acetate

N-Vinyl Pyrrolidone

Styrene

Vinyl Chloride

Acrylonitrile

Allyl

The examples are included to illustrate and not to limit this invention.

Well known free radical initiators include 2,2-Azobisisobutyronitrile, Acetyl Peroxide, Benzoyl Peroxide, t-Butyl Peroxide, Cumyl Peroxide, t-Butylhydro Peroxide, Cumylhydro Peroxide, Hydrogenperoxide-Ferrous Sulfate.

Said polymers containing sulfo group are generally prepared by one of the conventional free radical polymerizations such as solution polymerization, suspension polymerization, emulsion polymerization and bulk polymerization.

As used in this application, the technical term "sulfo group" is used generically, unless otherwise indicated, to mean the polymers in the form of free acids or salts of potassium, sodium, ammonium.

As used in this application, the technical term "sulfonate monomer" is used generically, unless otherwise indicated, to mean the monomers containing  $-\text{SO}_3\text{M}$  group, in which  $\text{M}=\text{H}-$ ,  $\text{K}-$ ,  $\text{Na}-$ ,  $\text{NH}_4-$ .

As used in this application, the technical term "polymer" is used generically, unless otherwise indicated, to mean the polymers such as homo-polymers, copolymers, terpolymers, tetrapolymers etc. which include the polymers prepared by any number of monomers. The technical term

"copolymer" is used generically, unless otherwise indicated, to mean the copolymers prepared by many monomers which are different from each other.

Said polymers containing sulfo group comprise the polymers formed by condensation polymerizations of Formaldehyde with the following sulfonate monomers.

Sulfonate monomers:

Aminotoluene Sulfonic Acid  
Aminophenol Sulfonic Acid  
2-amino-4-chloro-phenyl Sulfonic Acid  
2-amino-1-naphalene Sulfonic Acid  
1-amino,8-naphthol-3,5 disulfonic Acid  
Amino- naphalene Trisulfonic Acid  
Aminobenzene-2,5 - disulfonic Acid  
Distilbene amino Sulfonic Acid  
Phenol Sulfonic Acid  
Amino- naphthol disulfonic Acid  
Aminodiphenylamine Methane Sulfonic Acid

Said polymers containing sulfo group comprise the polymers formed by direct sulfonation or alkyl-sulfonation of polymers.

Sulfonation and alkyl-sulfonation reagents include sulfur trioxide and its complex, sulfuric or chlorosulfonic acid, sultone, acetyl sulfate.

Sulfonates substituted polymers include sulfonated polystyrene, sulfonated polysulfone, sulfonated melamine-formaldehyde resin, sulfonated phenol-formaldehyde resin, sulfonated urea-formaldehyde resin, sulfonated naphthalene-formaldehyde resin, sulfonated ethyl cellulose, sulfonated polyurethane, sulfonated polypropylene glycol, sulfonated polyethylene glycol.

Said compositions of said blends consist essentially of

- (i) Polyvinyl alcohol; and
- (ii) Polymers containing sulfo group.

In said compositions of said blends, there are polymers containing sulfo group, the quantity of which is from 0.01wt% to 60wt%, preferably from 0.1wt% to 50wt%, more preferably from 1wt% to 45wt%, and most preferably from 1wt% to 40wt%. used to prepare Said blends can be prepared by any of the conventional industrial processes for preparing polymer blends, of which the melt mixing process is more preferable.

Said films prepared from said blends may contain conventional film forming additives, wetting

agents, fillers, plasticizers, antioxidants, mold releasing agents, biocides, anti-blocking agents, defoamers, lubricants, etc. According to the compositions of said blends, the quantity of the additives are from 0.1wt% to 18wt%.

Said films can be prepared by any of the conventional film forming processes, of which solution cast, melt extrude, blown film are more preferable.

The water solving rate of said films can be controlled by varying the compositions of said blends. The water solving rate of said films depends directly on the weight per cent of the polymers containing sulfo group in said blends. The weight per cent of the polymers containing sulfo group in said blends controls the water solving rate of said films.

Polymer blends are known as "polymer alloys". A new polymer blend is a new polymer alloy or a new material. The method of controlling the water solving rate of said films prepared from said blends by varying the weight per cent of the polymers containing sulfo group in the composition of said blends mentioned above is unique.

That the water solving rate of said films prepared from said blends is controllable has not been known yet.

That the water solving rate of said films can be increased to 2.4 times of that of polyvinyl alcohol film at the temperature of 0° C has not been known yet.

Theoretically, the mechanism under which the water solving rate of said films can be controlled has not been known. Experiments show that the polymers containing sulfo group in said blends do accelerate the water solving rate of said films mentioned above. That sulfonation of polymers turns said films from non-water soluble into water soluble is probably the reason.

#### Example 1

| Compositions of Said Films [wt%] |               |    |
|----------------------------------|---------------|----|
| Polyvinyl Alcohol                | [1]           | 90 |
| Poly Sodium Styrene Sulfonate    | [2]           | 10 |
| Average Mw of [1]=               | 7,000-13,000  |    |
| Average Mw of [2]=               | 18,000-26,000 |    |

Two components are premixed and then palletized for blown film process at the temperature of 200° C.

#### Example 2

| Compositions of Said Films [wt%] |     |    |
|----------------------------------|-----|----|
| Polyvinyl Alcohol                | [1] | 80 |
| Poly Sodium Styrene Sulfonate    | [2] | 20 |

Average Mw of [1]= 7,000-13,000  
 Average Mw of [2]= 18,000-26,000

Two components are premixed and then palletized for blown film process at the temperature of 200° C.

#### Example 3

| Compositions of Said Films [wt%] |     |    |
|----------------------------------|-----|----|
| Polyvinyl Alcohol                | [1] | 70 |
| Poly Sodium Styrene Sulfonate    | [2] | 30 |

Average Mw of [1]= 7,000-13,000  
 Average Mw of [2]= 18,000-26,000

Two components are premixed and then palletized for blown film process at the temperature of 200° C.

#### Example 4

A film is cast from an aqueous polyvinyl alcohol solution, the concentration and the average Mw of which are 18wt% and 7,000-13,000, respectively. The solution is poured on a glass plate and is spread into an uniform film by a glass bar and is dried for 24 hours at the temperature of 45° C.

The dried film is peeled off from the glass plate.

Table 1: Controllable Water Solving Rate of Said Films

| Table 1 |      |                                  |                                    |
|---------|------|----------------------------------|------------------------------------|
|         |      | Compositions of Said Films [wt%] | Water Solving Rate at 15° C [Sec.] |
|         |      | A                                | B                                  |
| Exp. 4  | Film |                                  | 100                                |
|         |      |                                  | 14.2                               |
| Exp. 1  | Film | 90                               | 10                                 |
|         |      |                                  | 10.2                               |
| Exp.2   | Film | 80                               | 20                                 |
|         |      |                                  | 8                                  |
| Exp.3   | Film | 70                               | 30                                 |
|         |      |                                  | 3                                  |

A = Polyvinyl Alcohol, the average Mw of which is 7,000-13,000

B = Poly Sodium Styrene Sulfonate, the average Mw of which is 18,000-26,000

Film size = Length 4cm X Width 1cm X Thickness 0.03 mil

Pour 250cc water into a glass beaker of 500cc. Keep the water at the temperature of 15°C and under constant stirring. The water solving rate is recorded in sec., which is the time interval measured between the first moment when said film touches the surface and the second moment when said film disappears by visual inspection.

The water solving rates of Exp. 1 Film, Exp. 2 Film and Exp. 3 Film are 1.4, 1.8 and 8 times faster than that of Exp. 4 Film, respectively.

#### Example 5

| Compositions of Said Films [wt%] |     |      |
|----------------------------------|-----|------|
| Polyvinyl Alcohol                | [1] | 91   |
| Poly Sodium Styrene Sulfonate    | [2] | 9    |
| Propylene Glycol                 | [3] | 12.6 |
| Sodium C12-16 Olefin Sulfonate   | [4] | 1.7  |
| Dihydroxy Ethylphenol Amine      | [5] | 1.7  |

The components are premixed and then palletized for the blown film process at the temperature of 195° C.

#### Comparative Example

#### Example 5

| Compositions of Said Films [wt%] |     |      |
|----------------------------------|-----|------|
| Polyvinyl Alcohol                | [1] | 100  |
| Propylene Glycol                 | [3] | 12.6 |
| Sodium C12-16 Olefin Sulfonate   | [4] | 1.7  |
| Dihydroxy Ethylphenol Amine      | [5] | 1.7  |

The components are premixed and then palletized for the blown film process at the temperature of 198° C.

Table 2: Water Solving Rate at the temperature of 25° C

Table 2



|                  | Said Film Com positions [wt%] |   |    | Water Solving Rate at 25° C [Sec.] |
|------------------|-------------------------------|---|----|------------------------------------|
|                  | A                             | B | C  |                                    |
| Comparative Film | 100                           |   | 16 | 8.4                                |
| Exp.5 Film       | 91                            | 9 | 16 | 4                                  |

A = Polyvinyl Alcohol, the average Mw of which is 7,000-13,000

B = Poly Sodium Styrene Sulfonate, the average Mw of which is 18,000-26,000

C = Propylene Glycol 12.6wt%; Sodium C12-16 Olefin Sulfonate 1.7wt%;  
Dihydroxy Ethylphenol Amine 1.7wt%

Film size = Length 4cm X Width 1cm X Thickness 0.03 mil

Pour 250cc water into a glass beaker of 500cc. Keep the water at the temperature of 25° C and under constant stirring. The water solving rate is recorded in sec., which is the time interval measured between the first moment when said film touches the surface and the second moment when said film disappears by visual inspection.

The water solving rates of Exp. 5 Film is 2.1 times faster than that of Comparative Film at the temperature of 25° C.

Table 3: Water Solving Rate at the temperature of 0° C

| Table 3          |                               |   |    |                                   |
|------------------|-------------------------------|---|----|-----------------------------------|
|                  | Said Film Com positions [wt%] |   |    | Water Solving Rate at 0° C [Sec.] |
|                  | A                             | B | C  |                                   |
| Comparative Film | 100                           |   | 16 | 22.4                              |
| Exp.5 Film       | 91                            | 9 | 16 | 9.4                               |

A = Polyvinyl Alcohol, the average Mw of which is 7,000-13,000

B = Poly Sodium Styrene Sulfonate, the average Mw of which is 18,000-26,000

C = Propylene Glycol 12.6wt%; Sodium C12-16 Olefin Sulfonate 1.7wt%;  
Dihydroxy Ethylphenol Amine 1.7wt%

Film size = Length 4cm X Width 1cm X Thickness 0.03 mil

Pour 250cc water into a glass beaker of 500cc. Keep the water at the temperature of 0° C and

under constant stirring. The water solving rate is recorded in sec., which is the time interval measured between the first moment when said film touches the surface and the second moment when said film disappears by visual inspection.

The water solving rates of Exp. 5 Film is 2.4 times faster than that of Comparative Film at the temperature of 0°C .

I have illustrated this invention in detail. Now I claim my claims as follows:

1. The water soluble films are made from the novel polyblends of polyvinyl alcohol and the polymers containing the functional group of sulfonic acid or its salt of potassium, sodium and ammonium. The solving rate of said films can be controlled and is great at low temperature. Said films are made from the conventional industrial film forming process.
2. Said films of claim 1 wherein the polymers containing functional group of sulfonic acid or its salt of potassium, sodium and ammonium are homopolymers or copolymers through the radical polymerization containing the sulfonic monomers.
3. Said films of claim 1 wherein the polymers containing functional group of sulfonic acid or its salt of potassium, sodium and ammonium are made from polymerization of the formaldehyde with sulfonic monomers.
4. Said films of claim 1 wherein the conventional film forming additives are included.
5. Said films of claim 1 wherein the polyblends contain 0.1-60 weight per cent of the polymers containing the functional group of sulfonic acid or its salt of potassium, sodium and ammonium.
6. In claim 5 wherein the polyblends contain 1-40 weight per cent of the polymers containing the functional group of sulfonic acid or its salt of potassium, sodium and ammonium.
7. In claim 5 and claim 6 wherein based on the weight of the polyblends, it contains 0.1-18 weight per cent of the conventional film forming additives.
8. Said films of claim 1 wherein the polymers contain sodium sulfonic styrene.
9. In claim 7 wherein the polyblends contain 1-40 weight per cent of the polymers containing sodium sulfonic styrene.
10. In claim 9 wherein based on the weight of the polyblends, it contains 0.1-18 weight per cent of the conventional film forming additives.

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